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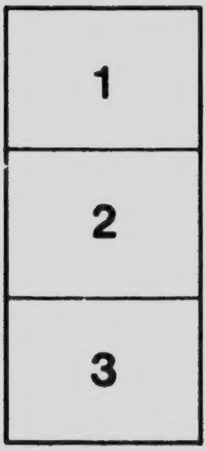

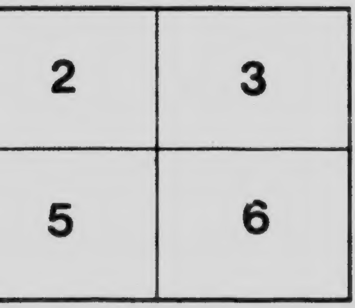

UNIVERSITY OF TORONTO STUDIES

PAPERS FROM THE CHEMICAL LABORATORIES

No. 62: THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE, β-NAPHTHOQUINONE, PHTHALONIC ACID AND PHTHALIC ACID, BY MAITLAND C. BOSWELL

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THE DETECTION AND ESTIMATION OF α-NAPHTHOQUINONE β-NAPHTHOQUINONE, PHTHALONIC ACID AND PHTHALIC ACID.

By Maitland C. Boswell.

Received December 8th, 1906.

During the progress of research upon the mechanism of the oxidation of naphthalene to phthalic acid, it was found necessary to be provided with methods for the detection and accurate determination of α-naphthoquinone, β-naphthoquinone, phthalonic acid and phthalic acid; and also with a method for the determination of phthalic acid in the mixture of organic acids formed by the oxidation. As no such methods are described in the chemical literature, I was forced to work them out for myself; and after a number of preliminary trials arrived at the following, which have proved very satisfactory, both as to the simplicity of the operations involved, and the accuracy of the results obtained.

Determination of α-Naphthoquinone: This compound was prepared by the method of Japp and Miller[1] which is an improvement on the method of Groves[2].

The reaction of the quinone which seemed best suited for the purposes of an analytical method is that with stannous chloride, which has been used by Plimpton[1] and by Russig[2] for the preparation of α-hydro-naphthoquinone and its derivatives.

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[1] J. Chem. Soc. **39**, 220 (1881).

[2] Liebig's Ann. **167**, 357, (1873).

In the first experiments I treated the quinone with a large quantity of the stannous salt, and attempted to determine the excess of the latter with decinormal iodine. No satisfactory results were obtained, however, either at room temperature, or at 100°. This might be accounted for by the action of iodine on the hydro-naphthoquinone formed by the reduction; but even when the latter was removed the results were still unsatisfactory.

The plan was then changed, and the stannous salt was added to the quinone from a burette until the reduction was complete, the end point being recognized by the absence of characteristic color reactions of the quinone. Two methods of working were studied, differing in the nature of the indicator chosen; both gave good results, and in each $2SnCl_2$ were required for one mol. of $C_{10}H_6O_2$.

First Method: A decinormal solution of stannous chloride in two per cent. hydrochloric acid[3] is run into the alcoholic solution of the quinone, until the yellow color of the latter is almost discharged. The addition of the stannous chloride is then proceeded with drop by drop, testing after each addition on a watch glass, with a drop or two of a mixture of equal volumes of phenyl-hydrazine and alcohol. So long as a trace of the quinone remains a bright pink color is formed[4] (Taken, 0.0700 g. quinone: found, 0.070 g.).

Second Method: To the alcoholic solution of the quinone, three or four drops of freshly distilled aniline are added, and the whole is boiled; whereupon it turns bright red[5]. Decinormal stannous chloride is then run in from a burette, heating to boiling after each addition, until the red color is completely discharged. If the end point has been over-stepped, a volumetric solution of the naphthoquinone may be used for titrating back. (Taken, 0.0700 g. quinone; found, 0.072 g.).

Purification of β-Naphthoquinone: This compound was prepared according to the method of Lagodzinski and Hardine[6], about 40 g. of crude quinone being obtained from 50 g. β-naphthol. No method could be found in the literature for the purification of this crude material, and attempts to recrystallize it from ether, alcohol, benzene, petroleum ether, acetone, chloroform, or mixtures of these, were unsuccessful.

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[1] J. Chem. Soc. 37, 635 (1880).

[2] J. pr. Chem. 170, 32 (1900).

[3] If the acid is too concentrated, some of Knapp and Schultz's amorphous compound may be formed, Ann. 210, 178 (1881).

[4] Ber. 17, 3026, (1884).

[5] J. Chem. Soc. 37, 635 (1880)

[6] Ber. 27, 3075 (1894).

The following method based on the reduction of the quinone to the corresponding hydroquinone and subsequent oxidation of the latter, however, effects a complete purification without loss of material.

Twenty grams of the crude, dark colored quinone is placed in a 500 cc. Erlenmeyer flask, 250 cc. of water saturated with sulphur dioxide is added, the flask is corked tightly and the whole shaken violently for about half a minute or until nearly all is dissolved. The shaking must not be continued too long or there will be a loss due to the separation of hydroquinone from the solution. The mixture is then quickly filtered by suction through a Buchner perforated funnel directly into a solution containing 60 grams potassium bichromate and 40 cc. conc. sulphuric acid in 1200 cc. water cooled to 5°–10°. The suction flask should be shaken with a circular motion during the filtration. The pure quinone falls to the bottom as a bright yellow orange precipitate and a black tarry residue remains on the filter. A second portion of twenty grams crude quinone may be dissolved in sulphurous acid as before, and filtered into the same oxidizing mixture without removing the quinone already there.

Determination of β-Naphthoquinone: Decinormal stannous chloride is added from a burette to the quinone dissolved in ether. A dark green, almost black, opaque solution results; owing, probably, to the formation of a quinhydrone. On adding more tin solution a point is finally reached at which the solution in ether suddenly becomes colorless and transparent, indicating the complete reduction of the quinone to hydroquinone. Each mol. quinone requires one mol. $SnCl_2$. (Taken, 0.0700 g.; found, 0.071 g.).

Purification of Phthalonic Acid: The syrupy solution prepared from naphthalene and potassium permanganate by the method of Graebe and Trümpy[1] crystallizes on long standing in a desiccator to a solid mass, said to consist of the dihydrate of phthalonic acid[2]; I found it, however, impossible to obtain a preparation of definite composition without completely dehydrating the acid. This is seen from the following determination of the water of crystallization.

1.9676 g. of the pulverized amorphous acid was heated in a steam bath for five hours; the loss in weight was 0.2116 g. It was further heated at 115° to constant weight. Total loss in weight, 0.2606 g.

	Found	Calc. ($C_9H_6O_5.2H_2O$)
H_2O	13.3	15.65

The acid thus contained 2.35% less water of crystallization than corresponds to the dihydrate.

Determination of Phthalonic Acid: Two methods were devised for the quantitative determination of phthalonic acid, both of which can be quickly and accurately carried out. In the first the carbon monoxide evolved on heating with sulphuric acid is measured, and the second the phthalonic acid is oxidized by a volumetric solution of potassium permanganate.

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[1] Ber. 31, 369, (1898).

[2] Ibid 370, (1898).

First Method: The phthalonic acid, about 0.5 g., is placed in a thick-walled hard glass test tube; and 5 cc. concentrated sulphuric acid is added. The tube is then fitted with a rubber stopper through which pass two glass tubes, one running to within three quarters of an inch of the surface of the acid and connected with a carbon dioxide apparatus, *B*, the other ending just flush with the bottom of the stopper and connected to the inlet tube of a Schiff's azotometer, *C*, containing 30% caustic potash solution. The air is completely expelled by allowing a rapid stream of carbon dioxide to pass through the apparatus, the potash solution during this operation being almost all in the levelling bulb *D*. When the air is all expelled the tube of the azotometer is filled with the potash solution, and the levelling bulb placed so that the surface of the potash in it is about level with the inlet tube of the azotometer, the mixture of phthalonic acid and sulphuric acid is gradually heated in a paraffine bath to 130° when carbon monoxide is quite rapidly evolved. This continues for about ten minutes when the evolution slackens. The temperature is now raised to 140° and in five minutes more the greater part of the carbon monoxide is evolved. At this temperature carbon monoxide would continue to be evolved very slowly for six or seven hours; but if the temperature is raised to 180° the remaining gas is quickly given off, and

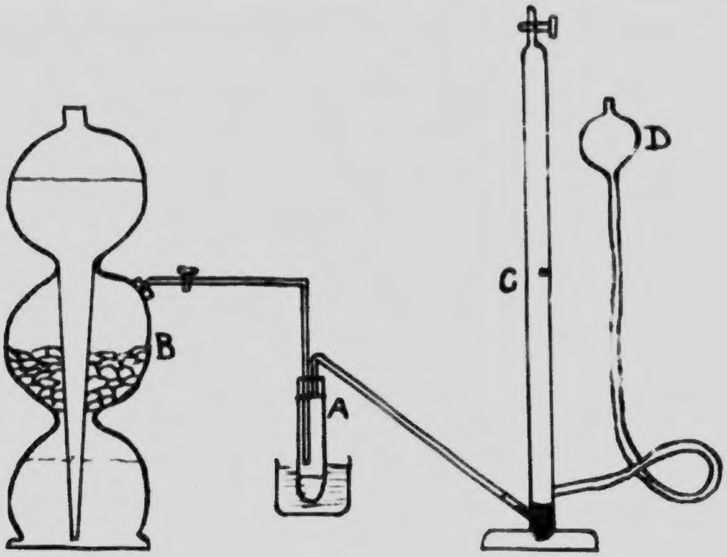

Fig. 1

the evolution entirely ceases. The whole duration of the heating is about one hour. The carbon monoxide remaining in the reaction tube is driven over into the azotometer by a stream of carbon dioxide; the levelling bulb is raised so that the pressure inside the azotometer is slightly greater than that of the atmosphere, and the azotometer is disconnected from the heating tube. The gas is then transferred to a gas burette filled with a saturated solution of carbon monoxide in water, and after standing half an hour the volume is read, barometer and thermometer being noted. In each of two experiments an amount of carbon monoxide corresponding to 0.49 g. of phthalonic acid was obtained from 0.500 g. of the acid.

Another series of experiments showed that when phthalic acid or phthalic anhydride was heated with concentrated sulphuric acid to 210°, no gas not absorbed by caustic potash solution was evolved.

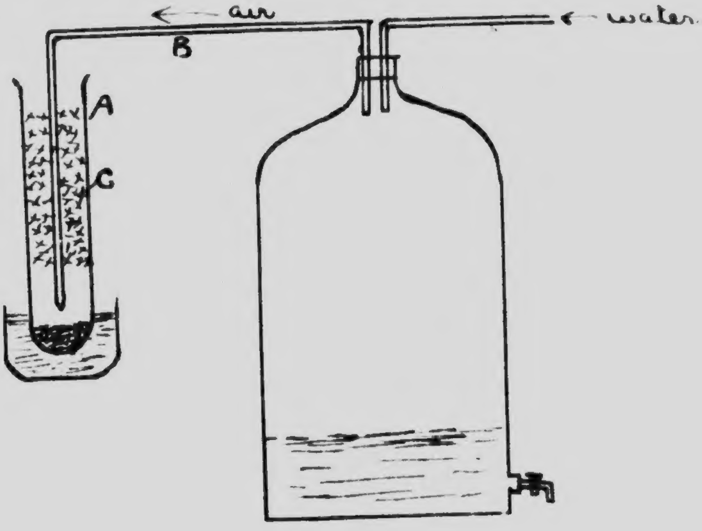

Fig. 2.

Second Method: This method, while just as accurate as the preceding has the advantage of being much more rapid; it allows the determination of phthalonic acid in the presence of phthalic, homophthalic, and phthalid-carbonic acids.

The phthalonic acid is dissolved in water, sulphuric acid added, and decinormal potassium permanganate run in from a burette. The oxidation is slow at first, but increases in speed as it proceeds, owing probably to the catalytic action of the manganous sulphate formed. The end point can best be obtained by running in an excess of permanganate and titrating back with ferrous sulphate until the last tinge of pink is discharged.

By working in this way the end point can be determined without difficulty within two drops of twentieth-normal ferrous sulphate. The results agreed accurately with the theory.

The titration must not be carried out in hot solutions, as in that case homophthalic, phthalid-carbonic, and even phthalic acids are acted on. By adding manganous sulphate to the phthalonic acid before running in the permanganate, the action of the latter is much accelerated.

Separation and Determination of Phthalic Acid: The method consists in separating the phthalic acid from homophthalic and phthalid-carbonic acids by sublimation, and determining it with volumetric alkali. The apparatus in which the sublimation is effected is made up of the test tube A, the air tube B, and the absorbent cotton C, to catch the sublimed phthalic anhydride. The tube B ends in a fine point about half an inch above the mixture of organic acids in the bottom of the test tube, and is connected with an inverted aspirator D.

The test tube is immersed to the depth of 3/4-inch in a metal bath kept at 200°–220°, and a fairly strong current of air directed on to the surface of the acids. After half an hour, the apparatus is removed from the bath. When cool, the bottom of the test tube is cut off, the cotton is transferred to a beaker and any anhydride adhering to the interior of A or the exterior of B is washed into the beaker by a volumetric solution of caustic potash. Excess of the potash is then added to the contents of the beaker, and after the cotton has soaked for half an hour in the alkaline solution, the excess of alkali is determined by volumetric sulphuric acid and phenol phthalein, boiling and taking the usual precautions to avoid errors due to carbon dioxide. A blank experiment showed that the "Bauer and Black cotton" used was perfectly neutral.

In this connection it should be noted, that phthalic anhydride cannot be determined by caustic potash in the presence of alcohol; even the alcohol contained in a few drops of phenolphthalein solution used as indicator affects the results, causing the red color to appear with too little potash, possibly due to the formation of an acid ester of phthalic acid. It is necessary, therefore, to introduce the indicator in the solid form, or dissolved in the volumetric potash.

The following results show the degree of accuracy of the method. Taken, 0.250 g. phthalic acid, 0.25 g. homophthalic acid and 0.25 g. phthalid-carbonic acid; found, 0.252 and 0.249 g. phthalic acid.

Fluorescein Reaction: This was carried out in the following manner: One decigram of resorcinol was mixed with its own weight or less of the acid to be tested, moistened in a test tube with one drop of concentrated sulphuric acid, and heated to 160° for three minutes in a bath of sulphuric acid. After cooling, the mass was shaken with 2 cc. of a 10 per cent. solution of caustic soda, and poured into 500 cc. of water.

When resorcinol alone is treated as described above, a red solution is obtained with marked blue fluoresence. One decigram of phthalic acid with the resorcinol gives a light solution with very strong green fluorescence; one milligram, a red solution with green fluorescence; and one-fifth milligram, a solution redder than the last, with blue-green fluorescence; on comparing it with the solution obtained from resorcinol alone, the green hue of the fluorescence is distinctly recognizable.

The following substances were also tested, one decigram being used in each case: naphthalene, red-pink solution, with green fluorescence; α-naphthoquinone, the same; β-naphthoquinone, dark green solution, no fluorescence; α-naphthol, red solution, blue fluorescence; β-naphthol, the same. In none of these cases was the fluorescence as marked as when one-fifth milligram of phthalic acid was employed. Phthalonic acid gave a dark red solution, with strong blue-green fluorescence; phthalid-carbonic acid, a pink-red solution with green fluorescence, much resembling that obtained from naphthalene; and homophthalic acid, a slightly red solution, with green fluorescence, almost as strong as when a decigram of phthalic acid was used.

I desire to express my thanks to Prof. W. Lash Miller under whose direction this work was performed.

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